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Long-range intramolecular electron transfer in aromatic radical anions and binuclear transition metal complexes

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Intramolecular electron transfer (ET) over distances up to about 10 Å between states in which the electron is localized on donor and acceptor groups by interaction with molecular or external solvent nuclear motion occurs, in particular, in two classes of systems. The excess electron in anionic radicals containing two aromatic end groups connected by a flexible polymethylene chain or a rigid cyclohexane frame is thus trapped on either aromatic end group, and ET between these groups can be detected by ESR techniques. Intramolecular ET also occurs in binuclear transition metal complexes in which the coupling between the metal centers [Ru(II)/Ru(III) and Ru(II)/Co(III) couples] is sufficiently weak (class I or II mixed valence compounds). The ET mechanism can involve either direct transfer between the donor and acceptor groups or a higher order mechanism in which ET proceeds through intermediate states corresponding to the localization of the electron on the interconnecting fragments. We have derived rate expressions for the different conceivable intramolecular ET pathways. In particular, we have incorporated the nuclear motion not only in the initial and final states but also in the intermediate states. We have furthermore provided criteria for the distinction between direct ET, ET through high-energy (superexchange), and low-energy ("radical" intermediate mechanism) intermediate states on the basis of experimental rate data and illustrated this with data for organic radical anions, and for intramolecular and inner sphere ET for transition metal complexes.

I. INTRODUCTION

Electron transfer (ET) between localized donor and acceptor centers separated by distances comparable to or exceeding the extension of the molecular framework of the reacting entities is of importance in the following contexts: (1) electron transport in biological membranes¹; (2) electron tunneling through the Schottky barrier of semiconductor electrodes^{2,3} and at metal electrodes covered by oxides,^{4,5} polymers,⁶ or molecular electrocatalysts^{7,8}; (3) ET involving solvated electrons in frozen glasses⁹; and (4) ET through extended bond systems as in inner sphere ET through bridge ligand systems^{10,11} or intramolecular ET between "molecular" trapping centers separated by a molecular chain.¹²⁻¹⁹ While the first three classes have been subject to fairly extensive investigations in terms of quantum mechanical nonadiabatic rate theory, the available analysis of the fourth class is much less comprehensive. Consideration of the fourth class in terms of multiphonon nonadiabatic rate theory adopted to incorporate both first and higher order perturbation effects is therefore the content of the present work. In particular, the following two groups of systems have been subject to experimental investigations: (A) Organic anionic radicals of diphenyl- and dinaphthylalkanes, -cycloalkanes, and related compounds¹²⁻¹⁷; these processes involve ET of the excess electron from one aromatic end group to the other, the donor and acceptor groups being separated by methylene groups, by an oxygen or a sulphur atom, or by a cyclohexane ring, and the rate constants were calculated from the broadening of the ESR signal of the excess electron; (B) binuclear transition metal complexes of the type $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{L} \cdots \text{LRu}^{\text{II}}(\text{NH}_3)_5$, in which $\text{L} \cdots \text{L}$ represents a pyridyl (=L) ring coordinated to either

metal center and containing molecular chains of varying length and flexibility between the rings^{18,19}; the intramolecular ET can here be measured by following the decay of the complex. These systems display close analogies to optical electronic processes in the "symmetric" binuclear ruthenium complexes containing localized Ru(II) and Ru(III) centers¹⁸⁻²¹ (class I and II mixed valence compounds²²), to inner sphere ET through extended bond systems,^{10,11} and to ET via extended ligand molecules in thermal outer sphere ET processes.²³

The long-range intramolecular ET may proceed by one of the following three mechanisms: (1) If the molecular chain which separates the donor and acceptor groups is sufficiently flexible, e.g., for a chain of methylene groups $-(\text{CH}_2)_n-$, where $n \geq 2$, the donor and acceptor groups can assume such a relative distance and orientation that direct ET is favorable^{16,17,19} (mechanism I).

For "short" ($n \leq 2$) or rigid molecular chains, unfavorable electronic overlap of the donor and acceptor orbitals may prevent direct ET. The process can then proceed by an indirect ("higher order") mechanism assisted by orbitals of the interconnecting molecular framework. Higher order ET then displays fundamentally different characteristics depending on the energy of the intermediate orbitals.

Thus, (2) for high-energy intermediate states the higher order nature of the process is essentially reflected in the pre-exponential factor of the resulting rate expression, whereas the activation energy coincides with that for direct ET (mechanism II). Distinction between direct ET and ET via high-energy intermediate states on the basis of experimental data must

then primarily be based on the different dependence of the pre-exponential factor on the lowest available energy levels of the intermediate electron mediating groups. ET via high-energy intermediate states corresponds to the mechanism of ET between transition metal centers analogous to magnetic superexchange suggested by George and Griffith²⁴ and expressed in terms of second order perturbation theory by Halpern and Orgel,²⁵ and to the mechanism for intramolecular ET in organic radical anions suggested by McConnell.¹³ However, Halpern and Orgel did not incorporate the nuclear motion, while McConnell only did so for the initial and final electronic states viewing the ET through the molecular chain as a purely electronic effect.

(3) For low-energy intermediate electronic states the system is actually temporarily accommodated in these states and could in principle be detected here (mechanism III). This would correspond to a "radical intermediate mechanism,"^{10,11} and the activation energy now also depends crucially on the energy level of the intermediate states which in principle provides a possibility of practical distinction from mechanisms I and II. We should notice that a single high order ET step via low-lying intermediate states is in principle different from consecutive direct ET steps involving the intermediate states since the latter mechanism—in contrast to the former—implies complete nuclear relaxation and statistical thermal averaging over all intermediate states subsequent to each ET step.

The intramolecular rate probability for ET between localized electronic states has more recently been considered in terms of propagator techniques which, however, essentially only included the electronic subsystem.²⁶ We shall now reformulate the intramolecular "higher order" ET mechanisms with special reference to radical anions and transition metal complexes. We shall generalize the formalism which was previously developed for second order ET processes via a single intermediate state^{27–29} and used to describe such processes as electrochemical ET via adsorbed molecules,³⁰ concerted proton transfer reactions,³¹ membrane processes,³² and inner and outer sphere ET.²³ In particular, in view of the small size of some of the intermediate groups, such as the methylene group, the coupling between the electronic and nuclear motion is expected to be important not only in the initial and final states, but also in all the intermediate states, and a further analysis of these effects will be the subject of the following

II. RATE EXPRESSIONS FOR HIGHER ORDER PROCESSES

Our formulation of the rate of intramolecular ET is an extension of the theory of second order ET processes involving intermediate states.^{29–32} In the nonadiabatic limit this formulation also displays some fundamental analogies to the theory of first order multiphonon transitions between a single donor and acceptor electronic level.^{32–39} The quantum mechanical approach towards higher order processes can thus be specified in the following way;

(A) The entire electronic–vibrational system is characterized by a set of zero order states corresponding to the localization of the electron not only on the donor and acceptor molecular fragments, but also on the "bridge" molecular fragments.

(B) The Hamiltonians in the initial, final, and intermediate states are in general different. In terms of scattering theory⁴⁰ higher order processes are multi-channel processes, whereas first order ET processes only involve an ingoing and an outgoing reaction channel.

(C) For each electronic state we can construct a many-dimensional Born–Oppenheimer potential energy surface determined by the nuclear displacements. If we restrict ourselves to a single electronic state in each channel, the electronic states are represented by electronic–vibrational wave functions of the form

$$\Psi_{\alpha}(\mathbf{r}, \mathbf{q}) = \varphi_{\alpha}(\mathbf{r}, \mathbf{q}) \chi_{\alpha I}(\mathbf{q}), \quad (2)$$

where φ_{α} and $\chi_{\alpha I}$ refer to the electrons and the nuclei, respectively, in the electronic state α ($\alpha = i, f, d, d', d'', \dots$, where "i" stands for initial, "f" for final, and the d 's for the various intermediate states) and for the vibrational quantum number I ($I = v, w, u, u', u'', \dots$ for $\alpha = i, f, d, d', d'', \dots$), and \mathbf{r} and \mathbf{q} are the sets of electronic and nuclear coordinates, respectively, where the latter refer to both the external continuous medium and the discrete intramolecular modes.

(D) Sets of vibronic levels of the nuclear potential surfaces, constituting the quantum mechanical initial, final, and intermediate states, can subsequently be found.

(E) A microscopic rate constant is derived by considering the system to be initially presented in a vibronic level belonging to the initial state potential surface. Residual interactions which were not included in the zero order Hamiltonians couple the initial level to a dense manifold of final levels leading to an irreversible decay process. The decay probability is generally expressed by the \mathcal{T} operator in the form⁴⁰

$$W_{fi} = \frac{2\pi}{\hbar} \sum_w |\langle \Psi_f(\mathbf{r}, \mathbf{q}) | \mathcal{T} | \Psi_i(\mathbf{r}, \mathbf{q}) \rangle|^2 \delta(E_{fw}^0 - E_{iv}^0), \quad (3)$$

where E_{iv}^0 and E_{fw}^0 are the total energies in the initial and final states and $\langle \dots \rangle$ and (\dots) denote integration with respect to the electronic and nuclear coordinates, respectively.

(F) By expanding the \mathcal{T} matrix in a perturbation series, the appropriate matrix elements \mathcal{T}_{fi} take the form of an infinite series in the residual perturbations of the reaction channels. The first and second order terms are thus

$$\mathcal{T}^{(1)} = V_i; \quad \mathcal{T}^{(2)} = \sum_{du} \frac{V_f | \Psi_{\alpha}(\mathbf{r}, \mathbf{q}) \rangle \langle \Psi_{\alpha}(\mathbf{r}, \mathbf{q}) | V_i}{E_{iv}^0 - E_{du}^0 + i\gamma} \quad (4)$$

($\gamma \rightarrow 0+$), where V_i and V_f are the perturbations, i.e., the difference between the exact and the Hamiltonian of the channel i and f , respectively.

(G) The macroscopic nonadiabatic transition probability is finally expressed in terms of a thermal average of the microscopic transition probabilities, the

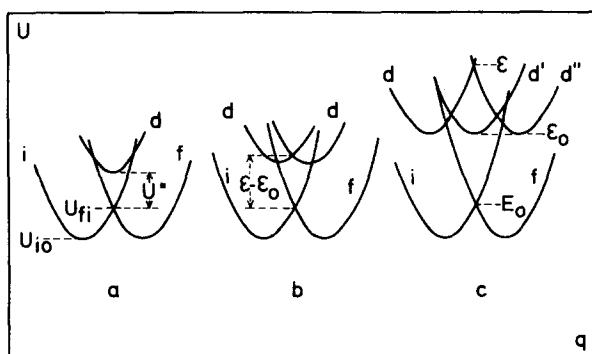


FIG. 1. One-dimensional potential energy surfaces for ET through one (a), two (b), and three (c) high-energy intermediate states: symmetric reactions.

Gibbs averaging being taken over the manifold of initial vibronic levels. This gives

$$W_{fi} = \frac{2\pi}{\hbar} Z^{-1} \sum_v \sum_w \exp(-E_i^0/k_B T) \times |\langle \Psi_f(\mathbf{r}, \mathbf{q}) | \mathcal{T} | \Psi_i(\mathbf{r}, \mathbf{q}) \rangle|^2 \delta(E_{iv}^0 - E_f^0), \quad (5)$$

where Z is the nuclear partition function in the initial state

$$Z = \sum_v \exp(-E_{iv}^0/k_B T). \quad (6)$$

In most considerations only the first order term is kept and inserted in Eq. (5). However, if this term is small or vanishing, the second or higher order terms will contribute preferentially. This is important in spin multiplicity-forbidden processes,⁴¹ or if the direct electronic overlap is small due to large separation between the donor and acceptor fragments, such as the intramolecular ET presently considered.

It is now convenient to consider separately the role of high- and low-energy intermediate states.

III. HIGH-ENERGY INTERMEDIATE STATES

The potential energy surfaces corresponding to the participation of one, two, and three high-energy intermediate levels are shown in a one-dimensional representation in Figs. 1(a), 1(b), and 1(c), respectively. The key feature is that the energy of the intersection region between the initial and final state surfaces, corresponding to direct ET between donor and acceptor, respectively, is lower than the energy of the intersection region corresponding to the transition to any of the intermediate states. The activation energy for the ET process is therefore determined by this point, and for sufficiently high energies of the intermediate states this means that the activation energy, but not the pre-exponential factor, depends relatively little on the number and nature of the links in the interconnecting chain. In addition, we notice the following about the representation of the process as in Fig. 1:

(a) The coordinate q represents the motion of both the collective solvent modes and the intramolecular (C-C skeletal or metal-ligand stretching) modes. As long as the electric field of the electronic charge distribution

causes a linear polarization response in the medium, the modes of the latter are well represented by harmonic motion subject to the equilibrium coordinate shift only. On the other hand, the intramolecular modes would commonly be subject to both vibrational frequency and equilibrium coordinate shifts. Finally, in contrast to low-energy intermediate states the results derived for high-energy intermediate states are essentially unaffected if the one-dimensional representation is replaced by a many-dimensional representation—in principle also when the medium is properly represented by a continuous mode distribution.

(b) in the construction of Fig. 1 and in the following we have assumed that the electron is localized in each intermediate state due to coupling to the vibrational motion. The condition for localization of the form⁴²

$$V_{\alpha\alpha'} \lesssim E_r^{\alpha\alpha'} \equiv \frac{1}{2} \hbar \omega_{eff}^{\alpha\alpha'} (q_{\alpha 0} - q_{\alpha' 0})^2, \quad (7)$$

where $V_{\alpha\alpha'}$ is the electron exchange energy for coupling of the electronic states α and α' , $E_r^{\alpha\alpha'}$ the reorganization energy (the "polaron shift energy") of all the nuclear modes for the ET step from α to α' , $q_{\alpha 0}$ and $q_{\alpha' 0}$ the equilibrium values of the nuclear coordinates in these two states, and $\omega_{eff}^{\alpha\alpha'}$ the effective vibrational frequency of all the nuclear coordinates.⁴³ This condition seems to be definitely satisfied for certain cases of binuclear metal complexes when either α or α' coincides with the initial and/or final state (cf. Sec. III). For the anionic radicals the large value of $V_{\alpha\alpha'}$ for covalent nearest-neighbor interaction makes the condition less obvious. However, due to the small geometric extension of the electron-mediating methylene groups, $E_r^{\alpha\alpha'}$ is also large in the strongly polar solvents, and may well be comparable to or exceed $V_{\alpha\alpha'}$. If the inverse of Eq. (7) is valid, the electron is not localized in the intermediate states. The ET then proceeds either via a single intermediate potential well, or directly from the donor to the acceptor group on a single potential surface with no intermediate potential well.

We can then invoke the Condon approximation separating the integrations with respect to the electronic and nuclear coordinates in Eqs. (3)–(5). For high-energy intermediate states the denominators furthermore depend weakly on the appropriate energies compared with the nuclear Franck-Condon overlap integrals which are left under the summation signs after removing the exchange integrals. The denominators can therefore be removed, leaving only the Franck-Condon factors. However, using the completeness rule, the summations over all the intermediate nuclear states gives a factor of unity and provide the rate expression as a product of an approximately constant electronic factor involving the electron exchange integrals of both the initial, final, and intermediate states and the energy denominators, and a thermally averaged Franck-Condon factor which contains the nuclear wave functions of the initial and final states only. The rate expression then only differs from those of two-level processes by the electronic factors, while the nuclear Franck-Condon factor is formally identical to those for two-level processes and can be handled by the theory of multiphonon processes.

More specifically, the rate expressions take the general form

$$W_{fi} = (\Delta U_{fi}^{(n)}/2)^2 A, \quad (8)$$

$$A = \frac{2\pi}{\hbar} Z^{-1} \sum_v \sum_w \exp(-E_{iv}^0/k_B T) \times |\langle \chi_{fw} | \chi_{iv} \rangle|^2 \delta(E_{iv}^0 - E_{fw}^0). \quad (9)$$

We now postpone the consideration of high-frequency nuclear modes (such as C-C and C-H skeletal modes or the high-frequency infrared part of the solvent modes) to Sec. V. The nuclear part A , which then represents the low-frequency modes (the greater part of the solvent modes or, for example, metal-ligand stretching modes) then takes the following form for rather general classical potential surfaces:

$$A \approx [(\pi \mu k_B T)^{1/2} / Z \hbar^2 2^{3/2}] \exp[-(U_{fi} - U_{i0} - \Delta U_{fi}^{(n)})/k_B T], \quad (10)$$

where μ is the effective mass associated with the motion on the low-frequency potential surfaces, U_{i0} the equilibrium energy of the initial state potential surface, and U_{fi} the energy of the saddle point of the initial and final state intersection surface (Fig. 1). The electronic factor which determines the splitting of the zero order surfaces in the intersection region between the initial and final state potential surfaces depends on the intermediate states. For the second order process, and provided that the direct interaction between the initial and final states can be ignored,

$$\Delta U_{fi}^{(2)} = 2V_{fd}V_{di}/(U^* - U_{fi}). \quad (11)$$

For the third order process [Fig. 1(b)]

$$\Delta U_{fi}^{(3)} = 2V_{dd'}|V_{d'i}|^2/[(\epsilon - \epsilon_0)^2 - |V_{dd'}|^2], \quad (12)$$

where we have explicitly incorporated the finite splitting between the two high-energy intermediate potential surfaces and, for the sake of simplicity, replaced the product of the exchange integrals $V_{fd}V_{dd'}V_{d'i}$ by $V_{dd'}V_{d'i}^2$. Similarly, for the (symmetric) fourth order process [Fig. 1(c)]

$$\Delta U_{fi}^{(4)} = 2|V_{dd'}|^2|V_{d'i}|^2/[(E_0 - \epsilon_0)(E_0 - \epsilon) - 2V_{dd'}^2](E_0 - \epsilon), \quad (13)$$

where we have only included nearest-neighbor interactions in the methylene chain.

The results derived so far are generally valid, i.e., for rather arbitrary potential energy surfaces and number of nuclear modes. Moreover, the validity of the nonadiabatic limit invoked only requires that the exchange integrals are small compared with the energy gaps between U_{fi} and the intermediate states, which allows for much larger values of the direct exchange integrals than for two-level processes. For the particular case when the initial and final states are represented by many-dimensional paraboloids subject to equilibrium coordinate shift only, A takes the form

$$A \approx (\pi/k_B T E_r \hbar^2)^{1/2} \exp\{-[(E_r + \Delta U_{fi}^0)^2/4E_r - \Delta U_{fi}^{(n)}]/k_B T\}, \quad (14)$$

where $\Delta U_{fi}^0 = U_{f0} - U_{i0}$ is the difference between the minimum energies of the initial and final state potential energy surfaces and E_r the total nuclear reorganization

energy, i.e., $E_r = \frac{1}{2} \sum_n \hbar \omega_n (q_{f0}^n - q_{i0}^n)^2$, where q^n is the n th nuclear mode, q_{i0}^n and q_{f0}^n the equilibrium values of q^n in the initial and final state, respectively, and ω_n the corresponding vibrational frequency. In particular, when the electron donor and acceptor centers are only coupled to the continuous solvent, ΔU_{fi}^0 is directly determined by the electron affinities and the solvation free energies of the appropriate groups, while the solvent reorganization energy is determined by the absorption spectrum of the medium in the classical frequency region ($\omega \lesssim 4k_B T/\hbar$) and by the electric field of the ionic charge distribution in the initial (D_i) and final (D_f) states, i.e.,^{39,44} (for a uniform medium)

$$E_r = \frac{e^2}{8\pi} \int (D_f - D_i)^2 dV \frac{2}{\pi} \int_0^{4k_B T/\hbar} \frac{\text{Im} \epsilon(\omega)}{\omega |\epsilon(\omega)|^2} d\omega = \frac{1}{2} \sum_n \hbar \omega_n (q_{f0}^n - q_{i0}^n)^2, \quad (15)$$

where $\epsilon(\omega)$ is the dielectric permittivity, V the volume, and e the electronic charge transferred.

IV. LOW-ENERGY INTERMEDIATE STATES

The handling of expressions such as Eqs. (3)–(5) is much more involved for low-lying intermediate states. In these cases the system also physically passes from the initial to the final state via the intermediate states. However, the energy liberated after the first transition is not dissipated but recovered for the continued passage to subsequent intersection regions. The rate expressions thus contain no averaging with respect to the intermediate states. The system is then expected to be present in the intermediate states for a period comparable to the relaxation time of the nuclear modes which span the potential surfaces. If the slow nuclear system is the modes of a low-molecular weight solvent, this time is of the order of 10^{-11} – 10^{-12} s and a possible detection would require rate measurements in the picosecond range. On the other hand, if conformational modes typical of macromolecular systems span the surfaces, the relaxation times may be larger by many orders of magnitude and therefore more suitable for experimental detection.

A quantum mechanical evaluation of Eq. (3) for low-lying intermediate states is only available for the second order component, for small perturbations (the non-adiabatic limit) provided that the electrons are strongly coupled to a low-frequency classical harmonic nuclear subsystem²⁸ or to a low-frequency harmonic and a set of separate high-frequency harmonic modes,⁴⁵ and provided that no mixing of the high- and low-frequency modes occurs during the process. However, several of these conditions are not likely to be met for some of the ET processes which we consider here. Thus, even if we need to consider coupling to the low-frequency medium modes only, we would still have to incorporate several intermediate states, corresponding to the localization of the electron on different orbitals of the methylene chain or cyclohexane bridge molecular framework. The exchange integrals between the different intermediate states are also substantial, so the nonadiabatic limit is inadequate. These effects have to be incor-

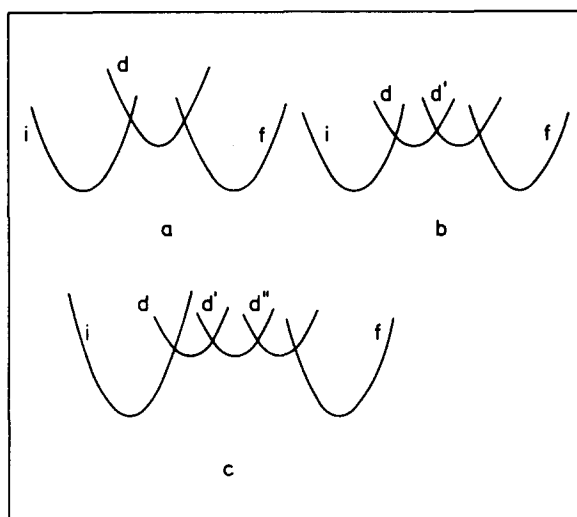


FIG. 2. One-dimensional potential energy surface for ET through one (a), two (b), and three (c) low-energy intermediate states: symmetric reactions and $U_{dd'}, U_{d'd''} > U_{id}, U_{df}, U_{d''f}$ in (b) and (c).

porated by means of an alternative, semiclassical procedure, i. e., by considering the classical motion of the system on the potential surfaces spanned by the nuclear modes and describing the electronic transitions in the intersection regions within the Landau-Zener formalism and extensions of this theoretical framework.²⁹

Semiclassical rate expressions for higher order processes through low-lying intermediate states are available for different model systems.²⁹ We consider at first a system characterized by a single low-frequency mode q and potential surfaces located as in Fig. 2. Provided that the system possesses sufficient energy, the overall probability of electronic transition by multiple passage of a given intersection point, e. g., at $U_{k,k+1}$, is

$$P_{k,k+1} = [1 - \exp(-2\pi\gamma_{k,k+1})] / [1 - \frac{1}{2} \exp(-2\pi\gamma_{k,k+1})]. \quad (16)$$

$\gamma_{k,k+1}$ is the Landau-Zener factor

$$\gamma_{k,k+1} = (\Delta U_{k,k+1}/2)^2 / \hbar v_{k,k+1} |U'_k - U'_{k+1}|^*. \quad (17)$$

$\Delta U_{k,k+1}$ is the splitting of the zero order potential surfaces in their intersection point, U'_k and U'_{k+1} the slopes (the derivatives with respect to q), $v_{k,k+1}$ the velocity of the system at this point, and the superscript "*" indicates that the derivatives are also taken at the intersection point. $P_{k,k+1}$ is thus a geometric sum of all transition probabilities for the individual passages.

When Eq. (16) is averaged with respect to the energy, the dominating contributions are provided by energies close to the highest of all the intersection points. If this point corresponds to the intersection of U_m and U_{m+1} , the averaged rate expression becomes

$$W_{fi} = \frac{\omega_{m,m+1}}{2\pi} \kappa_{m,m+1} \sum_{\substack{k \leq m \\ k > m}} P_{k,k+1} \times \exp[-(E_{A,m+1}^{m,m+1} + U_{m0} - U_{i0})/k_B T], \quad (18)$$

where the activation energy is the difference between

the energies of the intersection point between U_m and U_{m+1} ($E_{A,m+1}^{m,m+1} = U_{m,m+1} - U_{m0}$) and the equilibrium energy of the initial state U_{i0} . If the transition between U_m and U_{m+1} is strongly adiabatic, $E_{A,m+1}^{m,m+1}$ must be smaller than the value given by Eq. (18) by the amount $(\Delta U_{m,m+1})(U'_m U'_{m+1})^{1/2}/(U'_m + U'_{m+1})$, which is the value estimated as the maximum energy of the adiabatic potential energy surface relative to the intersection point of the zero order surfaces. Finally, in the nonadiabatic limit the transmission coefficient $\kappa_{m,m+1}$ is

$$\kappa_{m,m+1} = 2(\Delta U_{m,m+1}/2)^2 / [\hbar^2 (\omega_{m,m+1})^2 E_r^{m,m+1} k_B T \pi^{-3}]^{1/2}, \quad (19)$$

whereas $\kappa_{m,m+1} = 1$ in the adiabatic limit. Equation (18) is thus the transition probability during one period of motion $(2\pi\omega_{m,m+1}^{-1})$ on the potential surface U_m .

Equations (16)–(19) are also adequate for many-dimensional potential surfaces provided that the following modifications are invoked:

(1) The frequency $\omega_{m,m+1}$ is replaced by an "effective" frequency $\omega_{eff}^{m,m+1}$ which is determined by the reorganization energies along all the modes q_n . Thus, if a given mode q_n is associated with the frequency $\omega_n^{m,m+1}$ and a reorganization energy $E_n^{m,m+1} [= \frac{1}{2}\hbar\omega_n^{m,m+1}(q_{f0}^n - q_{i0}^n)^2$ for a harmonic mode] for the transition from U_m to U_{m+1} , then⁴³

$$(\omega_{eff}^{m,m+1})^2 = \sum_n (\omega_n^{m,m+1})^2 E_n^{m,m+1} / \sum_n E_n^{m,m+1}. \quad (20)$$

(2) The activation energy is generally no longer determined solely by the saddle point of highest energy, but also by the relative orientation of the potential surfaces.²⁹ We shall illustrate this with particular reference to a set of harmonic potential surfaces in which frequency dispersion effects are absent, i. e., all the (low-frequency) modes are characterized by a single value ω of the vibrational frequencies in both the initial, final, and all the intermediate states. This model is adequate when the two harmonic coordinates represent the outer solvent modes at high (i. e., room) temperature and in the "normal" energy gap region. Moreover, in order to keep the number of parameters as small as possible we invoke the plausible assumption that when more than one intermediate state participate, the zero order energies of the intermediate states are identical (as for a chain of methylene groups) and that the saddle point energies for transition between the various intermediate states are substantially higher than the saddle point energy from the initial (final) to the intermediate state d (d' or d''), i. e., $U_{dd'}, U_{d'd''} > U_{id}, U_{fd''}$. The activation energies for the overall process, whether it is symmetric or has a finite free energy of reaction, is then determined by the activation energy for transitions among the intermediate states, and separate consideration of symmetric and asymmetric processes may only be necessary for processes having a single intermediate state.

We consider at first a process which involves a single intermediate state. A suitable change of the coordinate axes of the potential energy surfaces then converts the many-dimensional surfaces spanned by all the (medium and intramolecular) coordinates to a set of two-dimensional surfaces spanned by the "collective" coordinates

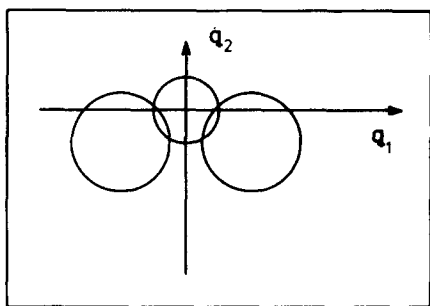


FIG. 3. Sections of two-dimensional potential energy surfaces at constant total energy: symmetric reactions and constant nuclear vibration frequencies along the coordinates q_1 and q_2 .

q_1 and q_2 ^{29,46} (Fig. 3):

$$U_i = \frac{1}{2} \hbar \omega (q_1 - q_{10}^i)^2 + \frac{1}{2} \hbar \omega (q_2 - q_{20}^i)^2 + U_{i0}, \quad (21a)$$

$$U_d = \frac{1}{2} \hbar \omega q_1^2 + \frac{1}{2} \hbar \omega q_2^2 + U_{d0}, \quad (21b)$$

$$U_f = \frac{1}{2} \hbar \omega (q_1 - q_{10}^f)^2 + \frac{1}{2} \hbar \omega (q_2 - q_{20}^f)^2 + U_{f0}, \quad (21c)$$

where q_{j0}^α ($j=1, 2$; $\alpha=i, f$) are the appropriate equilibrium values of q_1 and q_2 . Also, when the process is symmetric, then (a) $U_{i0} = U_{f0} < 0$ ($U_{d0} = 0$) and (b) $q_{10}^i = -q_{10}^f$ and $q_{20}^i = q_{20}^f$. Furthermore, for both symmetric and asymmetric processes the activation energy coincides with the energy of the highest saddle point only when (a) the minima of the potential surfaces are located on a straight line (i.e., $q_{20}^i = q_{20}^f = 0$) or (b) when the energies of the saddle points differ substantially, i.e., much more than $k_B T$.²⁸ In these cases the system passes from the initial to the final state via the intermediate state along a linear trajectory. We shall assume that this condition is valid for the asymmetric processes to be considered in the following (intramolecular ET in binuclear metal complexes). In these cases the activation energy is

$$E_A = (E_r^{di} + U_{d0} - U_{i0})^2 / 4E_r^{di}, \quad E_r^{di} = \frac{1}{2} \sum_{j=1}^2 \hbar \omega q_{j0}^{i2} \quad (22)$$

when the saddle point corresponding to the transition from the initial to the intermediate state has the higher energy. E_r^{di} is the total solvent and intramolecular reorganization energy corresponding to this step. Similarly, when the saddle point corresponding to the transition from the intermediate to the final state has the higher energy, the activation energy becomes

$$E_A = U_{d0} - U_{i0} + (E_r^{fd} + U_{f0} - U_{d0})^2 / 4E_r^{fd}, \quad E_r^{fd} = \frac{1}{2} \sum_{j=1}^2 \hbar \omega q_{j0}^{f2}, \quad (23)$$

where E_r^{fd} is the reorganization energy for the transition from the intermediate to the final state.

In all other cases the trajectory is curvilinear (Fig. 3), which implies that the activation energy is higher than either of the saddle point energies. The symmetric processes belong to this category for which we can derive the activation energy expressions in the following simplified way: With reference to Fig. 3 we notice that it is always possible to choose the coordinate system (q_1, q_2) in such a way that the activation energy is determined from the conditions

$$U_i = U_d, \quad q_2 = 0. \quad (24)$$

Inserting this in Eqs. (21a) and (21b) gives

$$E_A = E_{r2} + (E_{r2} - E_{r1} + U_{i0})^2 + U_{d0} - U_{i0}, \quad (25)$$

where E_{r1} ($= \frac{1}{2} \hbar \omega q_{10}^{i2}$) and E_{r2} ($= \frac{1}{2} \hbar \omega q_{20}^{f2}$) are the reorganization energies along the coordinates q_1 and q_2 , respectively. In comparison, the energies of either of the saddle points is $(E_{r1} + E_{r2} + U_{d0} - U_{i0})^2 / 4(E_{r1} + E_{r2}) < E_A$, and the total (medium and intramolecular) reorganization energy for each of the steps $i \rightarrow d$ and $d \rightarrow f$ is now $E_r = \frac{1}{2} \sum_{j=1}^2 \hbar \omega q_{j0}^{i2}$. The activation energy for the direct transition, i.e., not involving the intermediate state, would be $\frac{1}{2} \hbar \omega (2q_{10}^i)^2 = 4E_{r1}$.

ET involving two intermediate states requires four potential surfaces $i, d, d',$ and f analogous to Eqs. (21a)–(21c) [Fig. 2(b)]. Provided that the saddle point energy for the transition between the two intermediate states is substantially higher than the saddle point energy for transition from the initial (final) to the intermediate state $d(d')$, i.e., $U_{dd'} > U_{di}$, the activation energy is given by the highest saddle point, i.e.,

$$E_A = E_r^{dd'} / 4 - (U_{d0} - U_{i0}). \quad (26)$$

U_{d0} and $U_{i0} = U_{f0}$ (< 0) have the same meaning as before, and $E_r^{dd'}$ is the total reorganization energy in the transition from d to d' . We notice that the validity of Eq. (26) is not restricted to systems where frequency dispersion is absent.

For ET involving three intermediate states the initial, final, and intermediate states $d, d',$ and d'' , respectively, are now located as in Fig. 2(c). The saddle points for transitions between the three intermediate states correspond to equal energies but are likely to be located substantially higher than the saddle points for transition from $i(f)$ to $d(d'')$. The activation energy is therefore higher than the energy of the highest saddle points (i.e., the ones corresponding to transitions between the intermediate states). If frequency dispersion effects can be ignored, the many-dimensional intermediate potential energy surfaces can again be represented by two coordinates only q_1 and q_2 and the activation energy determined by a procedure identical to the one caused above for one intermediate state to give [cf. Fig. 3(b)]

$$E_A = \tilde{E}_{r2} + (\tilde{E}_{r2} - \tilde{E}_{r1})^2 / 4\tilde{E}_{r1} - U_{i0} = (\tilde{E}_{r1} + \tilde{E}_{r2})^2 / 4\tilde{E}_{r1} - U_{i0}, \quad (27)$$

where \tilde{E}_{r1} and \tilde{E}_{r2} are the reorganization energies for transition between two subsequent intermediate states, along the coordinates q_1 and q_2 , respectively [cf. Eq. (25)]. The quantity $U_{i0} = U_{d0} - U_{i0}$ in Eq. (25) would be $U_{d'0} - U_{d0} = 0$ for three intermediate states.

V. THE ROLE OF HIGH-FREQUENCY MODES

We have so far assumed that all nuclear modes behave classically, i.e., they are strongly thermally excited at room temperature and contribute fully to the activation energy. This assumption is adequate for the majority of the solvent modes in the processes considered. However, the ET is also likely to be accompanied by reorganization of intramolecular modes, such as C–H stretching and C–C skeletal modes, the frequencies

of which are so high (≈ 3000 and $1000\text{--}1500\text{ cm}^{-1}$, respectively) that the appropriate coordinate shifts proceed by nuclear tunneling. Provided that the discrete molecular modes constitute a set of normal coordinates separate from the low-frequency solvent modes, our previous approach would, however, still be valid. For each set of high-frequency nuclear vibrational quantum numbers in the initial, final, and intermediate states, a corresponding set of potential energy surfaces with respect to the low-frequency modes only can thus be defined. Provided that the splitting of the zero order surfaces in the intersection regions is small compared with the high-frequency vibrational energy level spacing, all transitions can be viewed as occurring independently, and the overall rate expression becomes (cf. Ref. 31)

$$W_H = \left(\prod_j Z_{v_j^i} \right)^{-1} \times \sum_{v_j^i, v_j^f, v_j^k} \exp(-\epsilon_{v_j^i}^i/k_B T) W_H(v_j^i, v_j^k, v_j^f) \prod_k S_{v_j^k, v_j^{k+1}}^{k, k+1}, \quad (28)$$

where v_j^α is the vibrational quantum number of the j th high-frequency mode in the electron state α , $\epsilon_{v_j^i}^i$ the corresponding energy, $Z_{v_j^i}$ the partition function of the j th mode in the initial state, $S_{v_j^k, v_j^{k+1}}^{k, k+1}$ the nuclear overlap function of the j th mode with respect to the states v_j^k and v_j^{k+1} and $W_H(v_j^i, v_j^k, v_j^f)$ the reaction probability [Eqs. (8), (9), and (18)] with the energy gap modified to incorporate given values of v_j^α . For the high frequencies of the intramolecular modes in the reactions considered presently we can, however, safely put all $v_j^\alpha = 0$. Incorporation of high-frequency molecular modes then only modifies Eqs. (8), (9), and (18) by the pre-exponential high-frequency Franck-Condon nuclear overlap factors of the ground vibrational states $\prod_k S_{0,0}^{k, k+1}$. (A more detailed analysis of the role of electronically or high-frequency vibrationally excited states for the adiabatic limit is given in Ref. 47).

VI. RELATION TO INTRAMOLECULAR ELECTRON TRANSFER SYSTEMS

Our formalism provides in principle a theoretical framework for the long-range intramolecular electron transfer in aromatic radical anions and in binuclear class I or class II transition metal complexes and related systems in which the donor and acceptor end groups are separated by rigid molecular residues which prevent a close approach of the groups. We notice the following implications of the theory;

(A) For ET through low-lying intermediate states the activation energy increases very strongly with increasing energy gap between the solvated donor and intermediate electronic levels. Moreover, the activation energy directly reflects the solvated electronic energy difference and the solvent properties via the energy quantities U_{i0} , U_{a0} , and E_r . On the other hand, both ET through high-energy intermediate states (superexchange) and direct ET between the donor and acceptor groups are expected to have activation energies which are largely independent of the energy gap involving the intermediate states.

(B) The activation energy increases, although weakly, with increasing chain length for both direct ET and ET through high-energy intermediate states. This is due to increasing solvent repolarization (E_r 's) with increasing ET distance. ET via low-lying intermediate states generally displays a more strongly increasing activation energy with increasing chain length [Eqs. (22)–(27)] due to the more involved trajectory on the increasing number of many-dimensional potential energy surfaces and the corresponding additional amount of energy required to pass the barriers.

(C) For ET through high-energy intermediate states the pre-exponential factor is expected to decrease approximately by a power law with both increasing energy gap between the intermediate and initial states, due to the appearance of the energy gap denominators, and with increasing number of chain links. This is analogous to the result derived by McConnell.¹³ In contrast, this dependence is exponential for direct ET, whereas the dependence of the pre-exponential factor on the number of links for ET through low-lying intermediate states is weaker due to the expected large electronic overlap and adiabatic character of the processes.

For a distinction between direct ET (mechanism I), ET through high-energy (mechanism II), and ET through low-energy (mechanism III) intermediate states on the basis of experimental data we emphasize in particular the following predicted behavior.

(a) The rate of direct ET only depends on the actual length of the molecular chain by the decreasing electronic overlap with increasing ET distance, i.e., through the pre-exponential factor. The activation energy depends on the energy gap between the donor and acceptor groups (but not on the energy of the bridge groups), and via E_r on the solvent properties in the same way as for ET between mobile donor and acceptor groups.

(b) Processes reacting by mechanism II displays basically the same activation energy dependence on the donor/acceptor energy gap and solvent as for direct ET. However, the pre-exponential factor decreases not only with increasing chain length, but depends also in a more detailed way on the lowest available energy levels of the electron mediating groups and the electron exchange integrals between these groups. Although both of these quantities generally vary with the nature of the molecular chain, the different dependence of the pre-exponential factor on the nature of the bridge groups would in principle allow a distinction between mechanisms I and II for a given class of systems.

(c) As noted above, in contrast to both mechanisms I and II, processes reacting by mechanism III show a pronounced dependence between the activation energy and the donor/bridge energy gap which would facilitate identification of this mechanism. In addition, variation of either the donor or the acceptor group might cause "structure" in the free energy relationship for the overall process due to the fact that ET from donor to bridge or from bridge to acceptor may both determine the overall rate and that a switch from one alternative to the other may occur within narrow free energy ranges.

The expectations listed above are in principle subject to experimental verifications, but the data available at present are unfortunately insufficient for detailed comparison. Among the earlier data for the α, ω -diphenylalkanes and related compounds, "fast" reactions ($\geq 10^7 \text{ s}^{-1}$) were thus observed when the number of methylene groups $n \leq 2$ and "slow" reactions ($\leq 10^7 \text{ s}^{-1}$) when $n > 2$.^{12,13} This observation is compatible with either mechanism I or II. It is notable that in the paracyclophane radicals, in which the benzene rings are oriented parallel to each other and connected by two methylene chains, the similar distinction between fast and slow processes is observed for larger n ($\approx 3-4$), which suggests a more favorable overlap for the direct ET.²⁰

We notice furthermore the following in relation to the role of the variation of the bridging and the end groups:

A. Variable molecular chain

Intramolecular ET rates in $\text{O}_2\text{N}\phi\text{-X-}\phi\text{NO}_2$ anion radicals in acetonitrile (ϕ = phenyl) have been reported to be (in s^{-1}) $\geq 10^8$, $\geq 10^8$, 2×10^8 [9×10^6 in dimethylsulphoxide (DMSO)], 1×10^6 (3×10^6 in DMSO), and $\leq 10^6$ (2×10^6 in DMSO) for $\text{X} = -, \text{CH}_2, \text{S}, \text{O}$, and CH_2CH_2 , respectively.¹⁴ The small difference between the rates of the O and S compounds, in spite of the widely different electron affinities, is compatible with either mechanism I or II and so is the pronounced decrease with increasing number of methylene groups.

Intramolecular ET rate parameters for the $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{L} \cdots \text{LRu}^{\text{II}}(\text{NH}_3)_5$ systems were reported by Taube and his associates.^{18,19} The activation energies were remarkably constant when groups of different length and flexibility were inserted between the pyridine rings, which excludes mechanism III. The activation entropy values (J K^{-1}) were 10.9 when no group was inserted, and 5.5, -12.1, -37.6, and -40.1 J K^{-1} when ethylene, sulfur, methylene, and ethane, respectively, were inserted. If we exclude the latter, for which mechanism I probably prevails due to the flexibility of the chain, the data indicate that ET most probably proceeds by mechanism II, i.e., ET through high-energy intermediate states. ET for the ethylene compound is thus faster by a factor of 10 than for the methylene compound in spite of the larger ET distance, probably caused by the more favorable electron exchange integrals and lower energies for the lowest bridge orbital [cf. Eq. (14)]. The same effect may be reflected in the difference between the activation entropies of the sulphur and the methylene compounds.

B. Variable end groups

The intramolecular ET rate between two naphthyl moieties linked together in the *para* positions of the rigid cyclohexane, i.e., *trans*-1,4-bis(α -naphthylmethyl) cyclohexane in hexamethylphosphorotriamide solution, is $9 \times 10^6 \text{ s}^{-1}$ at 15°C ^{17(a)} (compared with $4.4 \times 10^7 \text{ s}^{-1}$ in the conformationally flexible bisnaphthyl radical in which the naphthyl groups are separated by six methylene groups). For the analogous 1,4-bis(phthalimidoyl)cyclohexane radical the intramolecular

ET rate is only known to be smaller than $1 \times 10^8 \text{ s}^{-1}$ at 45°C ^{17(b)} (compared with $7 \times 10^7 \text{ s}^{-1}$ for the open chain hexamethylene radical). The intramolecular ET in the 1,3-bis(phthalimidoylmethyl)cyclohexane radical has the rate constant $4 \times 10^6 \text{ s}^{-1}$ at 15°C ^{17(b)} ($1.1 \times 10^7 \text{ s}^{-1}$ at 45°C), while the activation energy and pre-exponential Arrhenius factor are 25 kJ and $(5-10) \times 10^{10} \text{ s}^{-1}$, respectively (32 kJ and $4 \times 10^{12} \text{ s}^{-1}$, respectively, for the pentamethylene radical). If the 1,4 and 1,3 radicals have equal activation energies, the rate constant for the former at 15°C would be smaller than $4 \times 10^5 \text{ s}^{-1}$, i.e., lower than for the 1,4-bis-naphthyl compound by no less than a factor of 20. The electron affinities of naphthalene and phthalimide are 0.15 and 1.34 eV, respectively.^{48,49} Since the solvation energies of the two groups are approximately equal, the electron affinity difference provides a measure of the energy gap difference for ET from either group to an intermediate CH_2 group. These values would give both a far higher rate difference and a far higher activation energy than observed for these processes if the ET were mediated by low-lying intermediate states. On the other hand, the noticeable but slower dependence of the rate on the electron affinity difference, and the low value of the pre-exponential factor (suggesting nonadiabaticity) in the 1,3-substituted cyclohexane radicals, are compatible with ET through high-energy intermediate states. The fact that the larger electron affinity gives the lower rate further supports this [cf. Eqs. (11)–(13)], whereas direct ET between two groups of approximately similar geometry would depend weakly on their nature.

Nordmeyer and Taube reported inner sphere ET rate constants for the reaction between $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{M}(\text{NH}_3)_5\text{L}']^{3+}$, where L' is isonicotinamide^{10,11} and M is either Co (III) or Cr (III). They observed that the rate ratio for the Co (III) and Cr (III) complexes is only 17, whereas this ratio commonly exceeds 10^6 for small bridge ligands. This result was interpreted as a stepwise mechanism forced on the system by the mismatch of the acceptor orbital of σ symmetry and the bridge ligand orbital of π symmetry. According to the formalism of the present work the process would involve ET via a low-lying intermediate state (mechanism III). The first step is ET from Cr (II) to the reducible amide group. This step is followed by intramolecular ET to the Co center, and if the first step has the higher energy of the intersection region of the appropriate potential energy surfaces, the overall rate depends weakly on the energy of the second intersection region, i.e., on the metal center in this end.

The implications of mechanism III on free energy relationships with special reference to other Co (III)/Cr (II) systems were discussed in detail in Ref. 23(a).

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